Magnetic coupling and dynamics in solid α and β-O_2. II. Prediction of magnetic field effects

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Via simple thermodynamic arguments and via quantitative lattice dynamics and spin-wave calculations, we predict that the phase transition temperature $T_{\alpha\beta}$ in solid oxygen and the optical libron frequencies in the α and β phases will both be lowered by an external magnetic field. The lowering of $T_{\alpha\beta}$ varies from about 0.1 K at 7.5 T to about 1.2 K at 30 T. The lowering of the B_g and A_g libron peaks in the Raman spectrum of α-O_2 and of the E_g peak in the β-O_2 spectrum varies between 1.5 and 2.9 cm^{-1} at 30 T. These shifts can be explained by the magnetic field induced changes in the sublattice magnetizations, which affect the Heisenberg exchange contribution to the intermolecular potential. From *ab initio* calculations it is known that the Heisenberg coupling parameter J is extremely anisotropic.

I. INTRODUCTION

In the preceding paper I[1] we have discussed some properties of solid O_2, both as a molecular crystal and as a magnetic material. A lattice and spin-Hamiltonian has been derived from first principles and it has been shown that the dynamical and the magnetic properties of solid O_2 are directly related by coupling terms in the Hamiltonian which contain spin operators as well as structure dependent factors. Especially in the Heisenberg exchange term the dependence of the coupling parameter J on the positions and orientations of the molecules is very strong.[2,3] Lattice dynamics and spin-wave calculations that take into account these coupling terms yield good agreement with the measured magnon and libron frequencies in α and β-O_2. In particular, they explain the anomalously large libron splitting in α-O_2, which could not be understood from previous lattice dynamics calculations, but which appears to be caused by the extreme anisotropy of the Heisenberg coupling parameter J.[1,4]

The most direct demonstration of the importance of the coupling terms in our first principles Hamiltonian would be the measurement of an effect of external magnetic fields on some properties that are normally determined by a spin-independent intermolecular potential. Typical properties of this type are the phonon and libron frequencies and the transition temperature between different solid phases. In solid O_2 it should be possible to change the transition temperature between the α and β phases, as well as the libron frequencies in each of these phases, by applying an external magnetic field. The important question is, however, whether the changes are detectable for those field strengths that can be obtained in practice (up to about 30 T in static fields).[5] In the present paper we estimate the size of the magnetic field effects via theoretical calculations, in order to predict whether they will indeed be measurable.

II. THEORY

The theoretical framework for the calculations has been completely described in paper I. The Hamiltonian is defined by Eqs. (9)–(11). The spin-dependent terms, Eq. (9), are the Heisenberg exchange term, the intramolecular spin-orbit and spin–spin coupling term and the intermolecular spin–spin (magnetic dipole) coupling term. The dependence of the Heisenberg coupling parameter J on the positions and orientations of the molecules, Eqs. (3) and (35), has been obtained via *ab initio* calculations.[3] The geometry dependence of the other spin coupling parameters is well known, see Eqs. (6) and (8). Lattice dynamics and spin-wave calculations with this Hamiltonian start by the construction of separate mean field (MF) states for the molecular vibrations, translations, and librations, and for the spins, see Eqs. (14)–(16). Next, the correlation between the motions of the individual molecules as well as the coupling between the phonons, librons, and magnons is introduced via the random phase approximation (RPA), Eqs. (18)–(23).

The extension of this formalism for the calculations in the present paper is very simple. To the spin part of the Hamiltonian, Eq. (9), we have to add the Zeeman interaction:

$$H_Z = g_e \mu_B \sum_P \mathbf{B}\cdot\mathbf{S}_P \tag{1}$$

with the external magnetic field $\mathbf{B}$. Since this terms depends only on the single-molecule spins $\mathbf{S}_P$, we just need to add it to the MF Hamiltonian for the spins, Eq. (16). The MF states for the spins will thus be changed, and via the thermodynamic averages over the spin states in Eqs. (14)–(16), those for the translational vibrations and for the librations will change too. The RPA Hamiltonian (18), that yields the final phonon–libron–magnon states via Eqs. (19)–(23), will be affected via the excitation and deexcitation operators

$$a^{(K)\dagger}_{P,i_K} \text{ and } a^{(K)}_{P,i_K}$$

which are defined on the basis of the MF states. Just as in paper I, it is possible to make separate calculations for the lattice modes, the phonons and librons, and for the magnons, since there is very little mixing between these. The separation only occurs at the RPA level, however, and the coupling terms in the Hamiltonian have to be included in both calculations. In the spin-wave calculations they should be averaged over the (MF) molecular vibrations and in the lattice

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TABLE I. Magnetic susceptibilities (in 10^{-6} cm^3 g^{-1}).

	α-O_2				
	Calculated				Experiment (Ref. 6)
		$\chi_\perp$[a]			
T(K)	$\chi_\parallel = \chi_b$	χ_a	χ_{c^*}	χ	χ
5	0.9	262.0	253.6	172.2	48.1
10	3.3	262.0	253.6	173.0	48.6
15	21.2	262.0	253.7	179.0	50.6
20	56.0	262.0	253.8	190.6	55.5
22.5	76.7	262.0	253.9	197.5	60.1
	$\beta - O_2$				
	Calculated				Experiment (Ref. 6)
T(K)	χ_c	$\chi_a = \chi_b$	χ		χ
25	290.1	299.6	296.4		104.3
42	275.6	282.8	280.4		130.4

[a] Equation (2) yields $\chi_\perp = 262.2 \times 10^{-6}$ cm^3 g^{-1}.

dynamics calculations they must be averaged over the (MF) spin states. At specific points in the Brillouin zone of the structural Bravais lattice, for example at $\mathbf{q} = \mathbf{0}$, the phonons and librons in α- and β-O_2 do not mix either.

III. MAGNETIC PROPERTIES

Before looking at the α–β phase transition temperature and the libron frequencies in α and β-O_2, we first consider the response of the spin systems to external magnetic fields. The α phase is a two-sublattice collinear antiferromagnet with the sublattice magnetizations directed along the b axis of the monoclinic lattice. This preferential magnetization direction is usually imposed by a phenomenological spin Hamiltonian with two anisotropic single-particle spin terms, as in Eq. (1) of paper I. In paper I it is demonstrated, however, that it also follows from a spin Hamiltonian from first principles as in Eq. (9). Applying a small external field $\mathbf{B}$ in the b direction or perpendicular to it, we have calculated both the resultant overall magnetization and the free energy lowering and from both quantities we have extracted the magnetic susceptibilities $\chi_\parallel$ and $\chi_\perp$. This calculation has been performed at the MF level at various temperatures T, the results are given in Table I. Although we have included the anisotropic spin terms in the Hamiltonian of Eq. (9), paper I, the result for $\chi_\perp$ nearly satisfies the simple MF relation:

$$\chi_\perp = N g_e^2 \mu_B^2 |4J(\mathbf{0})^{\text{inter}}|^{-1} \tag{2}$$

which has been derived from the Heisenberg term only. The lattice sum $J(\mathbf{0})$ has been defined in Eq. (25) of paper I. The experimental data are given in Table I too and we observe that our calculated values of $\chi_\parallel$ and $\chi_\perp$ are considerably too high.

Also for β-O_2 the calculated susceptibility values are too high, by about the same factor, see Table I. In this phase the magnetic anisotropy within the ab plane is absent and all components of the susceptibility are nearly equal.

From the calculated sublattice magnetizations, as a function of temperature, we have derived the Néel temperature T_N of α-O_2. The relation $\chi_\parallel(T_N) = \chi_\perp(T_N)$ is approximately satisfied by the susceptibilities given in Table I, but not exactly because of the anisotropic spin terms in the Hamiltonian. The value $T_N = 49.5$ K thus obtained cannot be directly compared with experiment since the α phase is not stable above 23.9 K (at low pressure), but it is not far from estimated values.[6,7]

When α-O_2 is placed in a stronger magnetic field along the sublattice magnetization axis (the b axis) the spin momenta will change directions by about 90°. Experimentally, the so-called spin-flop field was found to be 7.5 ± 0.5 T.[8] In our calculations we can simulate this situation by increasing the field strength and we find the spin-flop field to lie at 7.1 T (at 0 K).

According to the simple relation (2) derived from MF theory the too high susceptibility values would indicate that the calculated Heisenberg coupling parameter J is considerably too small in absolute value. This has indeed been concluded in a recent paper.[9] We have evidence for the contrary, however. Our values of J, together with the well known free molecule values for the parameters in the anisotropic spin Hamiltonian from first principles, Eq. (9) of paper I, yield fairly good values for the optical magnon frequencies in α-O_2, which have been directly measured by infrared and Raman spectroscopy. Also the calculated Néel temperature and spin-flop field are quite realistic. Moreover, if the absolute value of J would be substantially in error, then the absolute values of its main anisotropic components would probably be incorrect too. The latter values enter directly into the calculated difference of the optical libron frequencies in α-O_2, which was found to be in very good agreement with the Raman spectra.[10,11] Actually, in paper I this libron splitting has, for the first time, been quantitatively explained. So we believe that the values of J extracted from the *ab initio* calculations[3] are not seriously in error, but that the error in the calculated susceptibilities will be mainly caused by the use of the mean field model.[12,13]

IV. THE α–β PHASE TRANSITION TEMPERATURE

The α phase of solid O_2 is stabilized with respect to the β phase by the magnetic interactions, in particular by the Heisenberg exchange coupling. So one expects that changes in the magnetic structure which may be caused by an external magnetic field will affect the phase transition temperature. From a simple thermodynamic argument we can derive a relation between the change in the phase transition temperature and the applied field strength. We start from the expression for the Helmholtz free energy differential:

$$dA = -S\,dT - p\,dV - M\,dB \tag{3}$$

with S being the entropy, T the temperature, p the pressure, V the volume, M the magnetization, and B the magnetic field strength as usual. We have to use[14] the form $-M\,dB$ for the magnetic contribution since the interaction of the magnetic dipole moments with the external field is explicitly included in the Hamiltonian, and thus in the free energy. Assuming that the magnetic susceptibility is field independent, we can write the free energy at field B as

$$A(B) = A(0) + \int_0^B \left[\frac{\partial A}{\partial B'}\right]_{T,V} dB'$$
$$= A(0) - \int_0^B \chi B'\, dB'$$
$$= A(0) - \tfrac{1}{2}\chi B^2 \qquad (4)$$

which holds for any temperature T. For temperatures close to the phase transition temperature $T_{\alpha\beta}$ we expand the free energy of the α phase as

$$A_\alpha(B,T) = A_\alpha(B,T_{\alpha\beta}) + (T - T_{\alpha\beta})\left[\frac{\partial A_\alpha}{\partial T}\right]_{B,T_{\alpha\beta}} \qquad (5)$$

while neglecting the higher order terms. Equation (4) can be directly substituted into the first term of Eq. (5) and it can also be put into the first derivatives:

$$\left[\frac{\partial A_\alpha}{\partial T}\right]_{B,T_{\alpha\beta}} = \left[\frac{\partial A_\alpha}{\partial T}\right]_{0,T_{\alpha\beta}} - \frac{1}{2}\left[\frac{\partial \chi_\alpha}{\partial T}\right]_{T_{\alpha\beta}} B^2$$
$$= -S_\alpha(T_{\alpha\beta}) - \frac{1}{2}\left[\frac{\partial \chi_\alpha}{\partial T}\right]_{T_{\alpha\beta}} B^2 . \qquad (6)$$

The same equations can be written for the β phase. Since, by definition:

$$A_\alpha(0,T_{\alpha\beta}) = A_\beta(0,T_{\alpha\beta}) \qquad (7)$$

and

$$A_\alpha(B,T) = A_\beta(B,T) , \qquad (8)$$

if T is the transition temperature in the external field B, we easily arrive at the following relation:

$$\Delta T = -\frac{\Delta\chi B^2}{2\Delta S + B^2 \Delta(\partial\chi/\partial T)} \qquad (9)$$

with

$$\Delta\chi = \chi_\beta(T_{\alpha\beta}) - \chi_\alpha(T_{\alpha\beta}) ,$$
$$\Delta S = S_\beta(T_{\alpha\beta}) - S_\alpha(T_{\alpha\beta}) ,$$
$$\Delta\left(\frac{\partial\chi}{\partial T}\right) = \left[\frac{\partial\chi_\beta}{\partial T}\right]_{T_{\alpha\beta}} - \left[\frac{\partial\chi_\alpha}{\partial T}\right]_{T_{\alpha\beta}} ,$$
$$\Delta T = T - T_{\alpha\beta} = T_{\alpha\beta}(B) - T_{\alpha\beta}(0) . \qquad (10)$$

By estimating the quantity $\Delta(\partial\chi/\partial T)$ from the measurements,[6,7,15] we have found that, for fields up to 30 T, the second term in the denominator of Eq. (9) may be safely neglected. Thus, the relation between the shift in the transition temperature and the applied field strength becomes simply

$$\Delta T = -\frac{\Delta\chi}{2\Delta S} B^2 . \qquad (11)$$

Both from experiment and from our calculations, see Table I, we know that $\Delta\chi > 0$, mainly because the parallel component of the susceptibility $\chi = \frac{1}{3}\chi_\parallel + \frac{2}{3}\chi_\perp$ is considerably smaller in the α phase. Since the calculated values for χ are not very reliable, we use the average experimental values of DeFotis[6]: $\chi_\alpha = 60.1\times10^{-6}$ cm^3 g^{-1} (at $T = 22.5$ K) and $\chi_\beta = 104.3\times10^{-6}$ cm^3 g^{-1} (at $T = 25$ K). Also the entropy change ΔS is positive, since the β phase is stable at higher temperatures; from the heat of transition, 92 J mol^{-1},[16] we calculate that $\Delta S = 3.85$ J mol^{-1} K^{-1}. Substituting these data into Eq. (11) we find that the α–β transition temperature is lowered by the magnetic field by an amount of 1.83 mK/T^2. At a field strength of 30 T the lowering of the phase transition temperature would thus be 1.65 K.

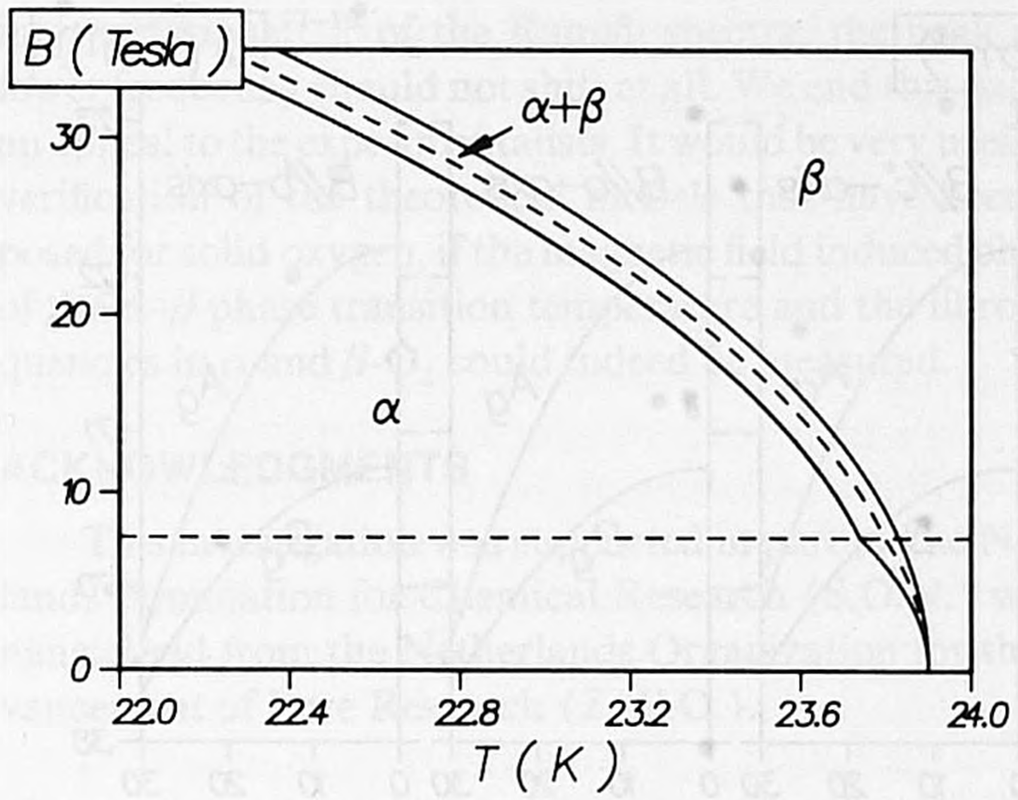

FIG. 1. Magnetic field strength dependence of the α–β phase transition temperature. The dashed curve depicts the average transition temperature. The solid curves indicate the range of transition temperatures in a powder sample. Note the effect of the spin flop in α-O_2 at 7.5 T.

The actual shift at higher magnetic field strengths will be smaller, however. At 7.5 T the α phase exhibits a spin flop which increases the parallel susceptibility component to about the same value as the perpendicular component, and thus decreases $\Delta\chi$. The effect of this spin flop on the change in $T_{\alpha\beta}$ is clearly visible in Fig. 1. The resulting ΔT is about 0.1 K at 7.5 T and about 1.2 K at 30 T, a small but possibly still measurable shift.

Another interesting phenomenon is observed by looking in detail at the anisotropy. In the β phase the susceptibility is nearly, but not exactly isotropic, see Table I. In α-oxygen $\chi_\parallel$, i.e., the component along the b axis, is about half of $\chi_\perp$ at the phase transition temperature.[6] Taking the susceptibility ratios from Table I, we estimate that the shifts in the transition temperature will be -2.88 mK/T^2 for a magnetic field along the b axis, -1.37 mK/T^2 for a field along the a axis and -1.25 mK/T^2 for a field along the c^* or c axis (the molecular axis). Such differences can only be measured in single crystals, of course. In powder samples the α–β phase transition in a magnetic field will take place over a range of temperatures, see Fig. 1.

V. MAGNETIC FIELD EFFECTS ON THE LIBRON FREQUENCIES

It has been suggested by several authors[10,17,18] that it would be useful to measure the Raman spectrum of solid O_2 in an external magnetic field. The reason for this suggestion was that the two peaks observed in α-O_2 could not be assigned in a satisfactory manner. It was believed that the peak at lower frequency contains two accidentally degenerate B_g and A_g libron modes. The peak at higher frequency should then correspond with a two-libron or libron–magnon transition[17,18] or with a libron or mixed libron–magnon mode which lies at the boundary of the Brillouin zone of the structural lattice but in the center of the magnetic Brillouin

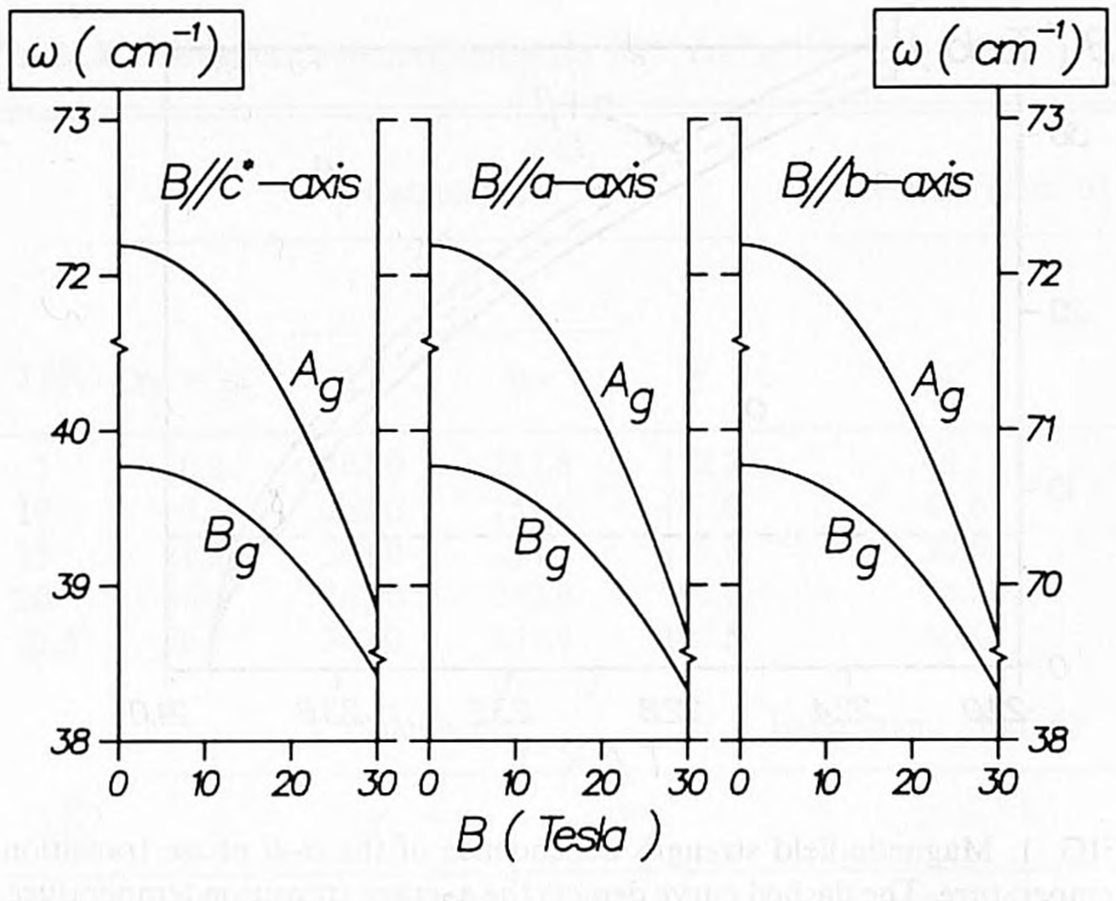

FIG. 2. Magnetic field induced lowering of the optical libron frequencies in α-O_2.

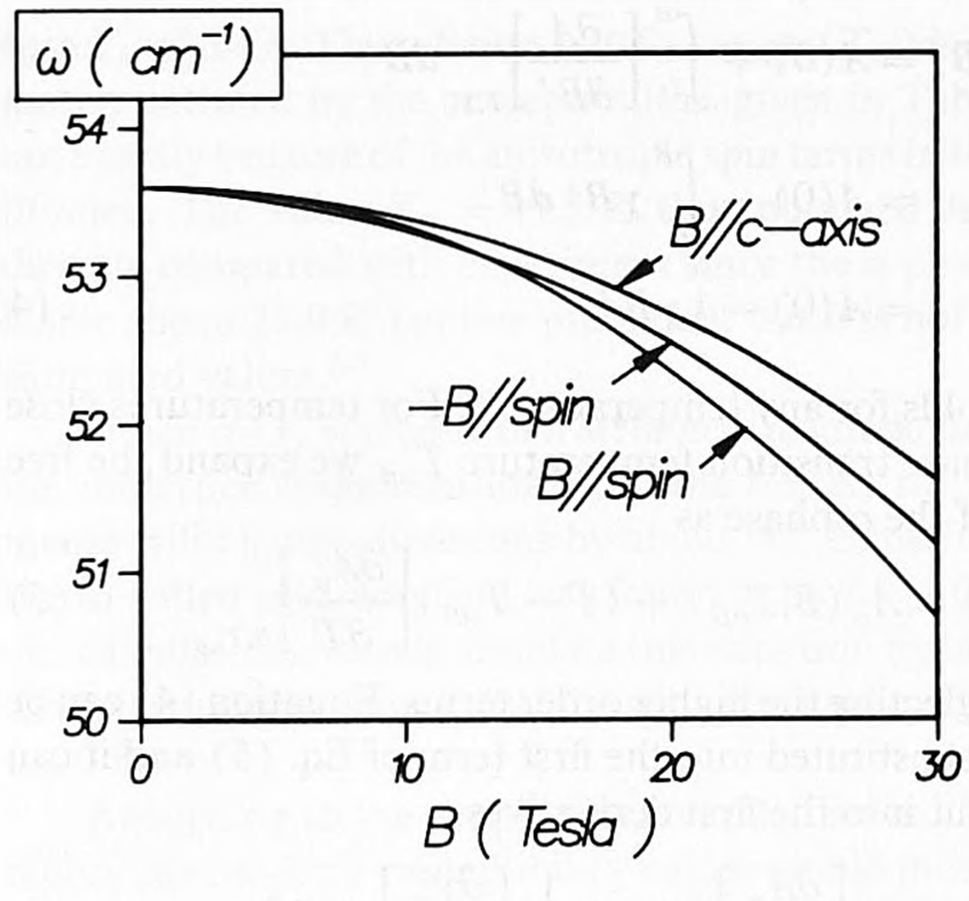

FIG. 3. Magnetic field induced lowering of the optical libron frequency in β-O_2. The lower two curves have been calculated with the field parallel or antiparallel to one of the sublattice magnetizations within the *ab* plane.

zone.[19] In a magnetic field the possible magnon character of these modes could be detected by a change of their frequencies, whereas pure libron modes would not shift.

In paper I and in Ref. 4 we have made a different assignment of the Raman spectrum on the basis of *ab initio* calculations.[3] The two peaks in α-O_2 have been identified as the B_g and A_g libron modes, respectively, and the large splitting was shown to be caused by the Heisenberg exchange term in the (spin-dependent) potential. So we think that both modes are pure libron modes, but that they will still be shifted by an external magnetic field which changes the magnetization and, thus, affects the spin factor $\langle \mathbf{S}_P \cdot \mathbf{S}_{P'} \rangle$ in the Heisenberg term. Here we report the explicit calculation of such shifts, as a function of the magnetic field strength, in α and β-O_2.

The calculations have been made as explained in Sec. II. Since we are mainly interested in the optical ($\mathbf{q} = \mathbf{0}$) libron modes which do not mix with the phonons, because of the symmetry in α and β-O_2, we have kept the centers of mass of the molecules fixed at the lattice sites. As it is primarily the Heisenberg exchange term from which we expect the libron shifts, we have retained the full geometry dependence of the Heisenberg coupling parameter J, as in Eqs. (3) and (35) of paper I, but we have replaced the anisotropic spin terms in the Hamiltonian of Eq. (9) in paper I by their semiempirical forms from Eq. (1), in order to simplify the calculations.

The magnetic structure of α-O_2 is fairly rigid. There is some frustration due to the antiferromagnetic coupling between the intralayer next-nearest neighbors which belong to the same sublattice. In a magnetic field the spins in the same sublattice will remain parallel, however, and thus this frustration cannot be removed. The magnetic order is further stabilized by the anisotropic spin terms, especially by the out-of-plane anisotropy. So one needs high fields to distort the magnetic structure to an appreciable extent and the resulting shifts in the libron frequencies will not be large. Figure 2 shows these shifts for the optical B_g and A_g librons. They amount up to 2.5 cm^{-1} for fields up to 30 T. They vary only slightly (by about 0.1 cm^{-1}) for different field directions, so that in a powder sample they should be measurable too. When the magnetic field lies along the *b* axis there is a discontinuity at 7.5 T, due to the spin flop. At this field strength the shifts are still too small for the discontinuity to be visible, however.

In β-O_2 we have assumed that the spins adopt the three-sublattice structure. The spin momenta lie in the *ab* plane, which situation is stabilized by the out-of-plane anisotropic spin terms. A magnetic field along the *c* axis gives the same *c* component to every spin. This distortion is not very favorable and the effect on the E_g libron frequency will be relatively small, see Fig. 3. If the field direction is parallel to the *ab* plane, the spin momenta can have all possible angles relative to this field. We have treated the extreme cases, i.e., we have placed the field parallel to one of the sublattice magnetizations or antiparallel to it. The three-sublattice order is a frustrated structure and it has been shown by several authors[20–22] that it can easily be distorted. We have found that this is indeed so, for fields parallel to the *ab* plane. The effects on the E_g libron mode frequency are displayed in Fig. 3.

Another interesting effect occurs in β-O_2 when we place the magnetic field parallel to the *ab* plane. The angles between nearest neighbor spins are no longer the same for all neighbor pairs. Via the average spin factors $\langle \mathbf{S}_P \cdot \mathbf{S}_{P'} \rangle$ in the Heisenberg exchange term the intermolecular potential differs for various neighbor pairs and the trigonal symmetry of the structural lattice is distorted. The unit cell of the distorted lattice contains three molecules. The Brillouin zone must be folded accordingly, and there will be phonons and librons at the zone boundary of the undistorted Brillouin zone that lie in the center of the distorted Brillouin zone. So, in a magnetic field parallel to the *ab* plane extra phonon or libron peaks may become visible in the infrared or Raman spectra. Their intensity will probably be small, however, as they differ only slightly from the phonons and librons that lie at the zone boundary in the absence of the field. Also the threefold symmetry axis has disappeared and the E_g mode will therefore be split. According to our calculations this splitting is small (less than 0.03 cm^{-1} for fields up to 30 T),

and so we expect the other symmetry breaking effects to be small too.

In Fig. 3 one can observe that for β-O_2 the shift of the E_g libron frequency depends rather strongly on the magnetic field direction. So, in powder samples we expect, in contrast with α-O_2, that the Raman peak will not only be shifted but also broadened by the magnetic field.

VI. CONCLUSION

We have quantitatively predicted the effects of external magnetic fields on the α–β phase transition temperature in solid oxygen, as well as on the libron frequencies in each of these phases. For the phase transition temperature $T_{\alpha\beta}$ we have used simple thermodynamic arguments to show that $T_{\alpha\beta}$ is lowered by the magnetic field, to such an extent that it might be measurable in the highest static magnetic fields that can be reached in practice (up to about 30 T). For the libron frequencies we have made quantitative calculations similar to those in paper I. The magnetic field induced shifts of these frequencies are caused by the Heisenberg exchange term in the spin-dependent lattice potential, via the extremely strong dependence of the coupling parameter J on the molecular orientations.

We have found the largest shift for the E_g libron frequency in β-O_2, when the magnetic field is parallel to the ab plane. It is questionable whether this shift (2.9 cm^{-1} at 30 T) can be measured, however, since the width of the observed Raman line[10] is 13 to 20 cm^{-1} and, in powder samples, this width will be further increased by the magnetic field. The shifts in the B_g and A_g libron frequencies are somewhat smaller (1.5 and 2.5 cm^{-1}, respectively, at 30 T) and the A_g peak is fairly broad too. Especially the shift in the lower frequency B_g peak, which has a linewidth of less than 1 cm^{-1}, should be visible in the Raman spectrum, however, even at somewhat weaker fields. According to the earlier interpretations[17–19] of the Raman spectra, the peak at the lower frequency should not shift at all. We end this paper by an appeal to the experimentalists. It would be very useful as a verification of the theoretical models that have been proposed for solid oxygen, if the magnetic field induced changes of the α–β phase transition temperature and the libron frequencies in α and β-O_2 could indeed be measured.

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